

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				213127US0PCT	
				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/914532	
INTERNATIONAL APPLICATION NO. PCT/EP00/01578		INTERNATIONAL FILING DATE 25 February 2000		PRIORITY DATE CLAIMED 8 March 1999	
TITLE OF INVENTION OLIGOMERIZATION OF C6-OLEFINS					
APPLICANT(S) FOR DO/EO/US MAAS Heiko et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 					
Items 13 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none"> 13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 22. <input type="checkbox"/> Certificate of Mailing by Express Mail 23. <input checked="" type="checkbox"/> Other items or information: 					
Notice for Consideration of Documents Cited in International Search Report/Notice of Priority PCT/IB/304/Amended Sheets (Pages 11 and 12) Drawings (1 sheet)					


U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.09/914532)	INTERNATIONAL APPLICATION NO. PCT/EP00/01578	ATTORNEY'S DOCKET NUMBER 213127US0PCT
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24. The following fees are submitted:.				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =					
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$80.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$860.00	
<input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$860.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$860.00	
				Amount to be: refunded	\$
				charged	\$

- a. ☒ A check in the amount of \$860.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

 22850 Surinder Sachar Registration No. 34,423

Surinder Sachar
SIGNATURE
Norman F. Oblon
NAME
24,618
REGISTRATION NUMBER
Aug. 30 2001
DATE

213127US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
HEIKO MAAS ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN :
(Based on PCT/EP00/01578)
FILED: HERewith :
FOR: OLIGOMERIZATION :
OF C6-OLEFINS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

3. (Amended) A process as claimed in claim 1, wherein the oligomerization is essentially a dimerization.
4. (Amended) A process as claimed in claim 1 carried out at from 30 to 300°C and a pressure in the range of from 10 to 300 bar.
5. (Amended) A process as claimed in claim 1 carried out continuously in the liquid phase.

7. (Amended) A process as claimed in claim 1, wherein the feed mixture is fractionated in a column to separate C₆-olefins and oligomers prior to the reaction, the C₆-olefins are returned to the reaction, the reacted mixture is returned to the column and the oligomers (C₇₊-hydrocarbons) are discharged.

8. (Amended) A process as claimed in claim 1, wherein the reacted mixture after the reaction is fractionated in a column to separate C₆-olefins and oligomers, the C₆-olefins are returned to the reaction and the oligomers are discharged.

9. (Amended) A process as claimed in claim 1, wherein the reaction is passed over a protective bed prior to the reaction.

REMARKS

Claims 1-9 are active in the present application. Claims 3-9 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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Marked-Up Copy

Serial No:

Amendment Filed on:

08/30/01

IN THE CLAIMS

--3. (Amended) A process as claimed in claim 1[or 2], wherein the oligomerization is essentially a dimerization.

4. (Amended) A process as claimed in [any of claims 1 to 3] claim 1 carried out at from 30 to 300°C and a pressure in the range of from 10 to 300 bar.

5. (Amended) A process as claimed in [any of claims 1 to 4] claim 1 carried out continuously in the liquid phase.

7. (Amended) A process as claimed in [any of claims 1 to 6] claim 1, wherein the feed mixture is fractionated in a column to separate C₆-olefins and oligomers prior to the reaction, the C₆-olefins are returned to the reaction, the reacted mixture is returned to the column and the oligomers (C₇₊-hydrocarbons) are discharged.

8. (Amended) A process as claimed in [any of claims 1 to 6] claim 1, wherein the reacted mixture after the reaction is fractionated in a column to separate C₆-olefins and oligomers, the C₆-olefins are returned to the reaction and the oligomers are discharged.

9. (Amended) A process as claimed in [any of claims 1 to 8] claim 1, wherein the reaction is passed over a protective bed prior to the reaction.--

as originally filed

1/pst

Oligomerization of C₆-olefins

- 5 The present invention relates to a process for oligomerizing C₆-olefins, in particular for preparing C₁₂-olefins by dimerization.

Processes for the oligomerization of olefins are known. DE-A-43 39 713 describes a process for oligomerizing olefins to give highly linear oligomers. In this process,
10 C₂₋₆-olefins are reacted at superatmospheric pressure and elevated temperature over a fixed-bed catalyst comprising from 10 to 70% by weight of nickel oxide, from 5 to 30% by weight of titanium dioxide and/or zirconium dioxide, from 0 to 20% by weight of aluminum oxide as significant active constituents and silicon dioxide as the remainder.

15 US 4,959,491 describes a process for dimerizing C₆-olefins to form C₁₂-olefins which can be used for preparing surfactants. Catalyst used are nickel-containing catalysts such as hexafluoro-acetoacetylnickel(cyclooctadiene).

20 DE-A-39 14 817 describes a process for oligomerizing C₂₋₈-olefins, in which the reaction is carried out over nickel-exchanged montmorillonite, a nickel-aluminum-silicon oxide catalyst or nickel-impregnated molecular sieves or zeolites. The olefin mixture used is passed over a molecular sieve prior to the catalytic reaction.

25 A disadvantage of the known processes is that the catalyst life is frequently too short. The catalyst is, in particular, clogged by higher oligomers and therefore loses its activity.

30 It is an object of the present invention to provide a process for oligomerizing C₆-olefins which avoids the disadvantages of the known processes.

We have found that this object is achieved by a process for oligomerizing C₆-olefins by reaction of a C₆-olefin-containing reaction mixture over a nickel-containing fixed-bed catalyst, wherein the reaction over the fixed-bed catalyst is
35 run at a conversion to oligomerized C₆-olefins of not more than 30% by weight, based on the reaction mixture.

The reaction over the fixed-bed catalyst is preferably carried out at a conversion of from 10 to 30% by weight, particularly preferably from 10 to 25% by weight, based on the reaction mixture. The oligomerization is preferably essentially a dimerization.

5

According to the present invention, it has been found that deactivation of the catalyst can be avoided and the dimer selectivity can be increased if the conversion over the catalyst is in the range indicated. The process can be carried out batchwise or continuously. It is preferably carried out continuously in the liquid phase. The conversion is then based on a throughput of the reaction mixture through the catalyst.

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The reaction is preferably carried out at from 30 to 300°C and a pressure in the range from 10 to 300 bar.

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In order to achieve a high total conversion in the process, part of the unreacted reaction mixture obtained can, after separating off the oligomers, be returned to the reaction. Adjustment of the recycled amount of reaction mixture enables very high total conversions to be achieved. The term "oligomers" includes dimers and higher-boiling compounds.

20

The process of the present invention makes it possible to realize a total conversion of over 90% together with a C₁₂ selectivity of over 80%. Adherence to the conversion specified according to the present invention over the catalyst (based on a single pass) greatly increases the operating life of the catalyst, since the formation of high-boiling compounds which can deposit on the catalyst and thus cause a drop in activity is suppressed.

25

C₆-olefins which are suitable for use in the process of the present invention can be synthesized on an industrial scale by methods such as propylene dimerization. The most important industrial propylene dimerization processes are described, for example, in A. Chauvel and G. Lefebvre, *Petrochemical Process*, Edition Technip (1989), pp. 183 to 187 and F. Asinger, *Die petrochemische Industrie*, Akademieverlag (1971), pp. 278 to 299. The oligomerization is carried out industrially in the presence of either homogeneous or heterogeneous catalysts. The heterogeneous catalysts which can be used are listed in, for example, C.T. O'Connor et al., *Catalysis Today* Vol. 6 (1990), pp. 329 to 349.

30

35

The most important, based on the amount produced, homogeneously catalyzed process is the Dimerol-G process of IFP. It is described in detail in Erdöl, Erdgas and Kohle, number 7/8, July/August 1990, pp. 309 to 315. The product obtained by means of this process (known as "Dimate") has the following average olefin composition:

C ₃ :	4% by weight
C ₆ :	73% by weight
C ₉ :	17% by weight
C ₁₂ :	4% by weight
C ₁₅₊ :	2% by weight

The C₆ fraction is composed of:

4-methyl-1-pentene:	0.9% by weight
2,3-dimethyl-1-butene:	2.3% by weight
cis-4-methyl-2-pentene:	3.1% by weight
trans-4-methyl-2-pentene:	21.7% by weight
2-methyl-1-pentene:	5.0% by weight
1-hexene:	0.3% by weight
trans-3-hexene:	4.4% by weight
cis-3-hexene:	0.7% by weight
trans-2-hexene:	13.6% by weight
2-methyl-2-pentene:	39.2% by weight
cis-2-hexene:	3.7% by weight
2,3-dimethyl-2-butene:	4.8% by weight

Another source of C₆-olefins is provided by metathesis processes.

Possible catalysts are generally nickel-containing catalysts known per se which give little branching, as are described, for example, in Catalysis Today vol. 6 (1990), pp. 336 to 338, DE-A 43 39 713, US 5,169,824, DD 2 73 055, DE-A-20 51 402, EP-A-0 202 670, Appl. Catal. 31 (1987), pages 259-266, EP-A-0 261 730, NL 8 500 459, DE-A-23 47 235, US 5,134,242, EP-A-0 329 305, US 5,146,030, US 5,073,658, US 5,113,034 and US 5,169,824.

In a preferred embodiment of the process of the present invention, the oligomerization is carried out in the liquid phase using the catalysts described in DE-A 43 39 713.

- 5 The catalysts described there consist essentially of nickel oxide, silicon oxide, titanium oxide and/or zirconium oxide and, if desired, aluminum oxide and have a nickel oxide content of from 10 to 70% by weight, a content of titanium dioxide and/or zirconium dioxide of from 5 to 30% by weight and an aluminum oxide content of from 0 to 20% by weight, with the remainder being silicon dioxide.
- 10 They are obtainable by precipitation of the catalyst composition at a pH of from 5 to 9 by addition of an aqueous solution of nickel nitrate to an alkali metal water glass solution containing titanium oxide and/or zirconium dioxide, filtration, drying and heating at from 350 to 650°C.
- 15 The catalysts preferably contain essentially from 10 to 20% by weight of titanium dioxide, from 0 to 10% by weight of aluminum oxide and from 40 to 60% by weight of nickel oxide as main constituent and active component and silicon dioxide as the remainder.
- 20 Especially preferred catalysts have the composition 50% by weight of NiO, 34% by weight of SiO₂, 3% by weight of Al₂O₃ and 13% by weight of TiO₂. They are largely free of alkali metals (Na₂O content < 0.3% by weight).

- The catalysts are preferably arranged in a fixed bed and are therefore preferably in
- 25 the form of discrete bodies, e.g. in the form of pellets (5mm × 5mm, 5mm × 3mm, 3mm × 3mm), rings (7mm × 7mm × 3mm, 5mm × 5mm × 2mm, 5mm × 2mm × 2mm) or extrudates (1.5mm diameter, 3mm diameter, 5mm diameter).

- In the process of the present invention, preference is given to reacting a
- 30 hydrocarbon stream comprising n-hexene and/or methylpentene, preferably in the liquid phase, over the abovementioned Ni-containing catalysts.

Suitable C₆-hydrocarbons are, for example, mixtures having the following composition:

- 35 paraffin: from 10 to 90% by weight
olefin: from 10 to 90% by weight,

where the olefin fraction can have the following composition:

n-hexenes: preferably from 0.1 to 99.8% by weight
methylpentenes: preferably from 0.1 to 99.8% by weight
dimethylbutenes: preferably from 0.1 to 99.8% by weight

5

The hydrocarbon streams used are advantageously freed of oxygen-containing compounds such as alcohols, aldehydes, ketones or ethers by adsorption using a protective bed such as molecular sieves, aluminum oxides, aluminum oxide-containing solids, aluminum phosphates, silicon dioxides, kieselguhr, titanium dioxides, zirconium dioxides, phosphates, carbon-containing adsorbents, polymer adsorbents or mixtures thereof, as is known per se from DE-A 39 14 817.

The oligomerization reaction takes place at from 30 to 300°C, preferably from 80 to 250°C and in particular from 100 to 200°C, and a pressure of from 10 to 300 bar, preferably from 15 to 100 bar and in particular from 20 to 70 bar. The pressure is advantageously chosen so that the feed mixture is in liquid form at the temperature set. The reactor is generally a cylindrical reactor or shaft oven charged with the catalyst and the liquid reaction mixture flows through it from the top downward. After leaving the single-stage or multistage reaction zone, the oligomers formed are separated from the unreacted C₆-hydrocarbons in a manner known per se (e.g. by distillation) and all or most of the latter is returned to the reaction (however, a certain purge to remove inerts, e.g. hexane, is always necessary).

A useful aspect of the method of carrying out the reaction provided by the present invention is the opportunity of carrying out the process adiabatically in a shaft oven, since the heat generated in the reactor can be controlled as desired by dilution of the hexenes with the recirculated stream by choosing the amount and temperature of this stream. Compared to an isothermally operated process, the adiabatic procedure leads to a considerable reduction in the capital costs of the apparatus.

In one embodiment of the invention, it is possible to fractionate the feed mixture in a column (K) to separate C₆-olefins and oligomers (C₇₊-hydrocarbons) prior to the reaction, to pass the C₆-olefins to the reaction (C1), to return the reacted mixture to the column (K1) and to discharge the oligomers (C₇₊-hydrocarbons).

In a further embodiment, it is possible to fractionate the reacted mixture after the reaction in a column (K1) to separate C₆-olefins and oligomers, to return the C₆-olefins to the reaction (C1) and to discharge the oligomers.

- 5 The two abovementioned variants are shown schematically in Figures 1a) and b) in the accompanying drawing.

In the figures, the symbols have the following meanings:

- 10 F1: protective bed
C1: reactor
K1: column
F: feed
P: purge
15 D: distillate
S: bottoms

The protective bed (F1) serves to remove catalyst poisons (essentially S-N-O-containing hydrocarbons).

- 20 The fractionation of the oligomers is carried out in a manner known per se by fractional distillation to separate off the desired dodecenes. The sulfur-free C₁₃₊ fraction displays a high blend value in respect of mixing into the diesel fuel pool. This C₁₃₊ fraction is particularly preferably used as diesel fuel component after the
25 olefins have been converted into paraffins by hydrogenation. This measure increases the cetane number which is a critical measure of the properties of the diesel fuel. All methods known from the prior art can be used for the hydrogenation.

- 30 The dodecenes obtained from the hexene dimerization can be further processed to produce surfactants.

The following examples illustrate the process of the present invention.

Examples

The experimental plant comprises the following plant items (process diagram as in Fig. 1):

- adsorber for removing catalyst poisons (F1, volume: about 50l)
- adiabatic reactor (C1, volume: about 40l, length: 8m, diameter: 80 mm)
- distillation column (K1) for separating unreacted C₆-olefins and the oligomers formed [C₁₂].

The catalyst used was a material which had been produced in the form of 5mm × 5mm pellets as described in DE-A 43 39 713. Composition in % by weight of the active components: 50% by weight of NiO, 13% by weight of TiO₂, 34% by weight of SiO₂, 3% by weight of Al₂O₃.

As adsorbent, use was made of a high surface area aluminum oxide such as Selexsorb[®] from Alcoa.

Example 1

The feed mixture used was a hydrocarbon mixture having the following composition:

C ₃ :	4% by weight
C ₆ :	73% by weight
C ₉ :	17% by weight
C ₁₂ :	4% by weight
C ₁₅₊ :	2% by weight

The C₆ fraction is composed of:

4-methyl-1-pentene:	0.9% by weight
2,3-dimethyl-1-butene:	2.3% by weight
cis-4-methyl-2-pentene:	3.1% by weight
trans-4-methyl-2-pentene:	21.7% by weight
2-methyl-1-pentene:	5.0% by weight
1-hexene:	0.3% by weight
trans-3-hexene:	4.4% by weight

	cis-3-hexene:	0.7% by weight
	trans-2-hexene:	13.6% by weight
	2-methyl-2-pentene:	39.2% by weight
	cis-2-hexene:	3.7% by weight
5	2,3-dimethyl-2-butene:	4.8% by weight.

The hydrocarbon mixture was introduced into the column K1 (Fig. 1) at a rate of 5.1 kg/h. The following conditions were set in the experimental plant:

<u>Adsorption section:</u>	
Pressure (bar)	15
Temperature (°C)	35
Throughput (kg/h)	18.8
<u>Synthesis section:</u>	
Amount of catalyst (kg)	25
Pressure (bar)	15
Inlet temperature (°C)	100
Outlet temperature (°C)	139
Throughput (kg/h)	18.8
<u>Distillation section:</u>	
Pressure (bar)	1
Temperature – top (°C)	35
Temperature – bottom (°C)	185
Amount fed in (kg/h)	23.9
Distillate (kg/h)	19.0
Purge (kg/h)	0.2
Bottoms (kg/h)	4.9

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The following result was achieved:

Composition

Stream	C ₃	C ₆	C ₉	C ₁₂	C ₁₅₊	Total C ₉₊
Feed mixture to K1 = reactor output	1.7	78.1	3.7	13.4	3.1	20.2
Distillate from K1	2.1	97.9	<0.1	<0.1	<0.1	-
Bottoms from K1	<0.1	0.4	17.7	64.7	17.2	99.6

5 This gives a C₆-olefin conversion of 94.7% and a C₁₂ selectivity of 83.6% (based on the C₆-olefins reacted).

Example 2

The feed mixture used was a hydrocarbon mixture having the following composition:

10

C₅: 0.9% by weight
C₆: 98.7% by weight
C₇: 1.2% by weight

15 The C₆ fraction is composed of:

4-methyl-1-pentene: <0.1% by weight
2,3-dimethyl-1-butene: <0.1% by weight
cis-4-methyl-2-pentene: <0.1% by weight
20 trans-4-methyl-2-pentene: <0.1% by weight
2-methyl-1-pentene: <0.1% by weight
1-hexene: <0.1% by weight
trans-3-hexene: 90% by weight
cis-3-hexene: 10% by weight
25 trans-2-hexene: <0.1% by weight
cis-2-hexene: <0.1% by weight
2-methyl-2-pentene: <0.1% by weight
2,3-dimethyl-2-butene: <0.1% by weight.

30 The hydrocarbon mixture was introduced into the filter F1 (Fig. 2) at a rate of 3.20 kg/h. The following conditions were set in the experimental plant:

<u>Adsorption section:</u>	
Pressure (bar)	10
Temperature (°C)	35
Throughput (kg/h)	3.20
<u>Synthesis section:</u>	
Amount of catalyst (kg)	25
Pressure (bar)	10
Inlet temperature (°C)	100
Outlet temperature (°C)	133
Throughput (kg/h)	15.75
<u>Distillation section:</u>	
Pressure (bar)	1
Temperature – top (°C)	45
Temperature – bottom (°C)	182
Amount fed in (kg/h)	15.75
Distillate (kg/h)	12.60
Purge (kg/h)	0.05
Bottoms (kg/h)	3.15

The following result was achieved:

Composition

5

Stream	C ₅	C ₆	C ₇₋₁₁	C ₁₂	C ₁₃₊	Total C ₇₊
Feed mixture to K1 = reactor output	<0.1	80.6	0.4	15.7	3.3	19.4
Distillate from K1	0.1	99.9	<0.1	<0.1	<0.1	-
Bottoms from K1	<0.1	0.4	1.3	81.2	17.1	99.6

This gives a C₆-olefin conversion of 98.4% and a C₁₂ selectivity of 82.6% (based on the C₆-olefins reacted).

as enclosed to IPER

We claim:

1. A process for oligomerizing C₆-olefins by reaction of a C₆-olefin-containing reaction mixture over a nickel-containing fixed-bed catalyst, comprising from 10 to 70% by weight of nickel oxide, from 5 to 30% by weight of titanium dioxide and/or zirconium dioxide and from 0 to 20% by weight of aluminum oxide as significant active constituents and silicon dioxide as the remainder, wherein the reaction over the fixed-bed catalyst is run at a conversion to oligomerized C₆-olefins of not more than 30% by weight, based on the reaction mixture.
2. A process as claimed in claim 1, wherein the reaction over the fixed-bed catalyst is run at a conversion to oligomerized C₆-olefins of from 10 to 30% by weight, based on the reaction mixture.
3. A process as claimed in claim 1 or 2, wherein the oligomerization is essentially a dimerization.
4. A process as claimed in any of claims 1 to 3 carried out at from 30 to 300°C and a pressure in the range from 10 to 300 bar.
5. A process as claimed in any of claims 1 to 4 carried out continuously in the liquid phase.
6. A process as claimed in claim 5 which is carried out adiabatically in a shaft oven and in which part of the reacted mixture is returned to the reaction.
7. A process as claimed in any of claims 1 to 6, wherein the feed mixture is fractionated in a column to separate C₆-olefins and oligomers prior to the reaction, the C₆-olefins are returned to the reaction, the reacted mixture is returned to the column and the oligomers (C₇+hydrocarbons) are discharged.

8. A process as claimed in any of claims 1 to 6, wherein the reacted mixture after the reaction is fractionated in a column to separate C₆-olefins and oligomers, the C₆-olefins are returned to the reaction and the oligomers are discharged.
9. A process as claimed in any of claims 1 to 8, wherein the reaction is passed over a protective bed prior to the reaction.

FIG.1A

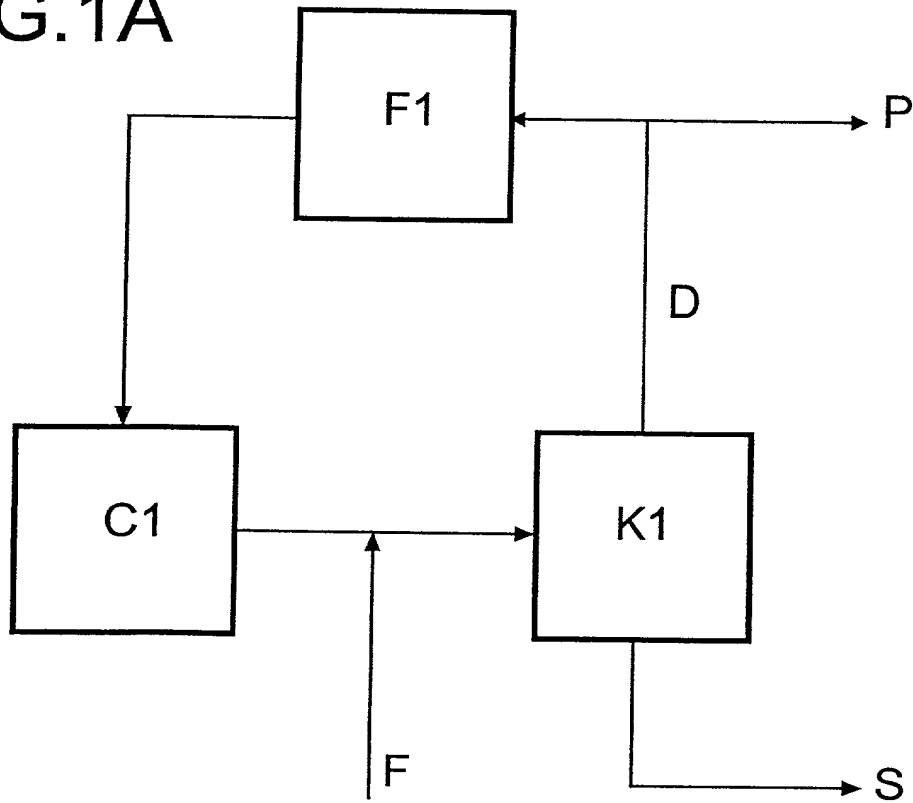
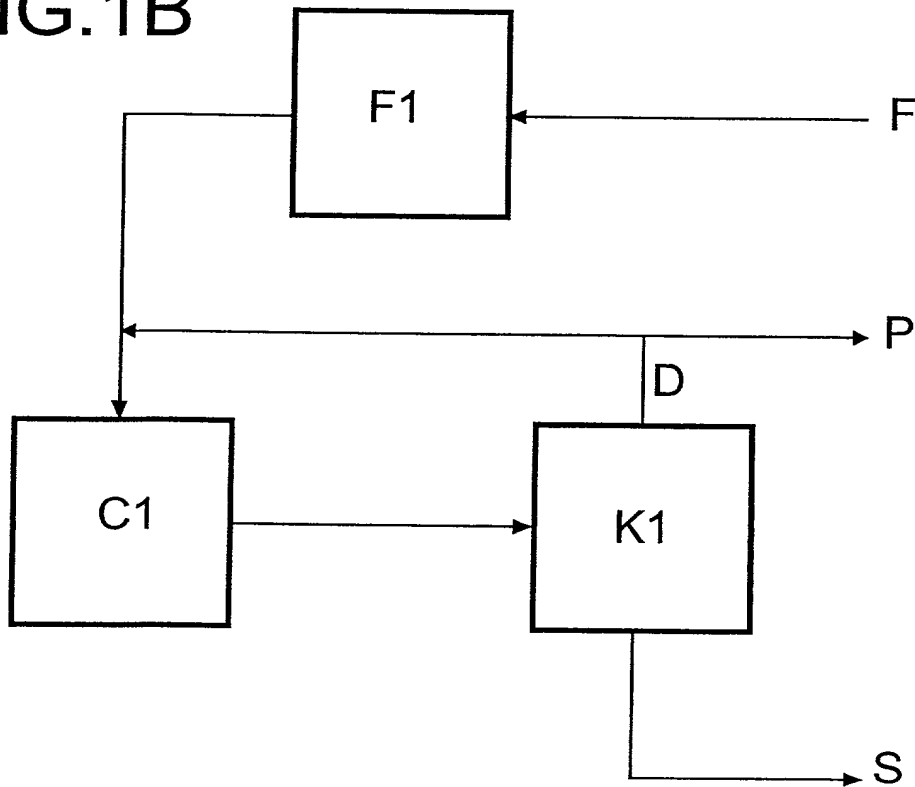


FIG.1B



Declaration, Power of Attorney

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We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Oligomerization of C6-olefins

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number _____ PCT/EP00/01578

on _____ February 25, 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19910103.5	Germany	08 March 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

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We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)
_____	_____
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; William E. Beaumont, Reg. No. 30,996; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; William T. Enos, Reg. No. 33,128; Michael E. McCabe, Jr., Reg. No. 37,182; Bradley D. Lytle, Reg. No. 40,073; and Michael R. Casey, Reg. No. 40,294; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Declaration

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